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CLUSTER DYNAMICS: LAYING THE FOUNDATION FOR TAILORING THE DESIGN OF CLUSTER ASSE

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14. ABSTRACT
Our overall goal is to establish the groundwork for using clusters as the building blocks of new materials with tailored properties that are beneficial to the AFOSR. Our continuing program is composed of two interrelated themes: the first comprises the investigation of fundamental physical and chemical properties of cluster building blocks in isolation, while the second involves the study of cluster deposition and assembly, including optical and chemical characterization of the formed materials. The ability to tune the pertinent properties of matter would facilitate the design of devices that could behave ideally in a specific application. Our objectives are outlined as follows: 1. Explore the electronic and geometric structure of clusters to enable the design of stable motifs for use in high energy-density materials and nanocatalysis. 2. Characterize dynamical processes to allow the precise control of building block reactivity on the atomic scale. 3. Extend the formalism for describing the interactions of clusters in rarefied environments to build a methodology for treating deposited clusters. 4. Examine the intra and inter cluster length scale interactions of deposited clusters to determine how the properties of the nanoscale material emerge.

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Contract/Grant #: FA9550-10-1-0071, P01

Reporting Period: April 15, 2014 – October 14, 2015

Final Accomplishments:

In order to understand the foundation for tailoring the design of cluster assembled materials, our research continues to investigate the electronic structures of small metal clusters and metalloids, and their role in cluster stability, reactivity, and mimicry. The final reporting period was focused on the rare earth mimicry and the properties of clusters containing Al, B, and Ag elements.

As an extension of our superatom concept, in the last year we have shown evidence in rare earth mimicry. We provided direct experimental evidence that the neutral LaB and NdB clusters have similar unpaired electrons and magnetic moments as their isovalent Nd and Eu rare earth elements, respectively. Extension of the superatom concept into the rare earth group will be of great importance in designing novel building blocks in the application of cluster-assembled nanomaterials. Additionally, a new experimental strategy is proposed to significantly increase the yield of the rare earth anions, providing the best opportunity to complete the periodic table of the atomic anions.

Other reactivity work has focus on the energetic aluminum boride clusters. The $Al_{12}B^-$ and $Al_{11}B_2^-$ clusters are found to be resistant to reactivity with O_2 due to their closed electronic shell, making them potential candidates to form cluster assembled solids. Other detailed studies were conducted during the past year have led to the discovery of C-S bond activation in the reaction of silver cluster anions with ethanethiol, which may offer insight into the mechanism by which ligand-protected clusters could be synthesized.

Publications During Current Grant Period:

*Publication in press after the April 2013-2014 progress report, listed here for final citation.

*707. "Photoelectron Imaging Spectroscopy of NbN-: Exploring Similarities with its Isovalent Analogues ZrO- and Pd-", C. Berkdemir, K. D. D. Gunaratne, S. Cheng and A. W. Castleman, Jr., *Physical Chemistry Chemical Physics, (submitted 2013)*.

*711. "Assigning the Mass Spectrum of NbN^-: Photoelectron Imaging Spectroscopy and Nominal-mass Counterpart Analysis." C. Berkdemir, S.B. Cheng and A.W. Castleman, Jr., *Int. J. Mass spectrom.*, **365-366** 222-224 (2014).

712. "Reactivity of Silver Clusters Anions with Ethanethiol", Z. Luo, G. U. Gamboa, M. Jia, A. C. Reber, S. N. Khanna and A.W. Castleman, Jr., *Journal of Physical Chemistry Special Issue A. W. Castleman, Jr. Festschrift*, **118**, 8345-8350 (2014).

713. "Special and General Superatoms", Z. Luo and A.W. Castleman, Jr., *Acc. Chem. Res.*, **47**, 2931-2940 (2014).

714. "Boron Substitution in Aluminum Cluster Anions: Magic Clusters and Reactivity with Oxygen", J. Smith, A. Reber, S. Khanna and A.W. Castleman, Jr., *Journal of Physical Chemistry Special Issue A. W. Castleman, Jr. Festschrift*, **118**, 8485-8492 (2014).

715. "Direct Experimental Observation of Weakly-Bound Character of the Attached Electron in Europium Anion", Shi-Bo Cheng and A.W. Castleman, Jr., *Scientific Reports,* **5** 12414 (2015).

716. "Mass Spectrometry and Its Role in Advancing cluster Science", P. Jena and A.W. Castleman, Jr., *IJMS,* **377**, 235-247 (2015).

717. "Joint Photoelectron Imaging Spectroscopic and Theoretical Characterization on the Electronic Structures of the Anionic and neutral ZrC2 Clusters", Shi-Bo Cheng and A. W. Castleman, Jr., *J. Phys. Chem. A,* **118**, 6935-6939 (2014).

718. "Mimicking the magnetic properties of rare earth elements using superatoms", Shi-Bo Cheng, C. Berkdemir and A. W. Castleman, Jr., *PNAS,* **112**, 4941-4945 (2015).

719. "On the Electronic Structure of the Diatomic VO anion: A Combined Photoelectron Imagining Spectroscopic and Theoretical Investigation", Shi-Bo Cheng, C. L. Harmon and A. W. Castleman, Jr., *J. Phys. Chem. A.,* (submitted 2015).

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1.

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Principal Investigator Name

The full name of the principal investigator on the grant or contract.

A. Welford Castleman, Jr.

Program Manager

The AFOSR Program Manager currently assigned to the award

Michael Berman

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Abstract

Our overall goal is to establish the groundwork for using clusters as the building blocks of new materials with tailored properties that are beneficial to the AFOSR. Our continuing program is composed of two interrelated themes: the first comprises the investigation of fundamental physical and chemical properties of cluster building blocks in isolation, while the second involves the study of cluster deposition and assembly, including optical and chemical characterization of the formed materials. The ability to tune the pertinent properties of matter would facilitate the design of devices that could behave ideally in a specific application. Our objectives are outlined as follows: 1. Explore the electronic and geometric structure of clusters to enable the design of stable motifs for use in high energy-density materials and nanocatalysis. 2. Characterize dynamical processes to allow the precise control of building block reactivity on the atomic scale. 3. Extend the formalism for describing the interactions of clusters in rarefied environments to build a methodology for treating deposited clusters. 4. Examine the intra and inter cluster length scale interactions of deposited clusters to determine how the properties of the nanoscale material emerge.

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Supplies			
Total			

Report Document

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Appendix Documents

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